Effects of Nucleating Agents on Preparation of Polypropylene Hollow Fiber Membranes by Melt Spinning Process[†]

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Abstract : Microporous polypropylene hollow fiber membrane was fabricated from isotactic polypropylene-soybean oil system by melt spinning process. Addition of nucleating agent accelerated the crystallization rate and elevated the crystallization temperature. Nucleating agent increased the number of nuclei and spherulites, which offered more inter-spherulitic amorphous sites for stretching. Benzoic acid, adipic acid, and dibenzylidene sorbitol were selected as nucleating agents, and their characteristics and effects were investigated by thermal and optical analyses. Spherulite growth and micropore formation characteristics were correlated with the kind of nucleating agent. Benzoic acid and adipic acid showed the remarkable nucleating effect, while dibenzylidene sorbitol was less effective than those. Nucleating agents also helped the sample have uniform microporous structure. Increase of nucleating agent composition enhanced the nucleation effect to some extent. Nucleating agents played very important roles in enhancing the membrane porosity and water flux.

Keywords : melt spinning, stretching process, isotactic polypropylene, nucleating agent, hollow fiber membrane.

Introduction

Polyolefin membranes have been applied to various fields of industry, and some fabrication methods were developed. One of its fabrication methods is thermally induced phase separation (TIPS) process, and several attempts have been made to control the microporous structure of the membrane.[1-5] In TIPS process cooling control has been regarded as the most important factor in determining the microporous structure. Phase separation mechanism mainly depends on thermodynamic interaction, but cooling condition can also affect the phase separation mechanism as well as the phase separation rate.[2,6,7] Several operation parameters in melt spinning process have been intensively investigated and were correlated with the structure of the hollow fiber membrane.[3-5] Hollow fiber membrane is usually stretched during the melt spinning process, and it helps formation of micropores in the amorphous region between crystalline phases. Stretching usually enhances the molecular orientation and crystallinity of the fiber, which have great influences on the micropore formation.[8] Therefore, crystallization behavior during the melt spinning and stretching is very important in determining the microporous structure.

Crystallization of semicrystalline polymer from its melt state mainly depends on the cooling conditions. However, nucleating agent (NA) addition also has great influence on the crystallization rate, crystallization temperature and crystal size.[9,10] Nucleating effects for semicrystalline polymers have been much investigated for the pure polymer systems. Effects of nucleating agent on the formation of crystalline phases were investigated for isotactic polypropylene system.[11] Mechanical properties of polypropylene blend system were enhanced by addition of nucleating agent.[12] Nucleation kinetics for polymer/diluent systems have been examined for isothermal and non-isothermal crystallization.[13-16] Effects of NA addition to the polymer-diluent system were examined in terms of morphology change of microporous membrane formation via TIPS.[17] Addition of NA decreases the free energy for nucleation, and it initiates the crystallization at higher temperature than non-nucleated system.[18] Uniform spherulite size distribution with more grainy core shape is obtained from nucleated system. NA helps chain folding to result in the increase of lamella thickness and crystallinity.[19] NA usually increases nucleation density and, therefore, number of spherulites. Spherulite growth is suspended by impingement on each other and increase of number of spherulites by NA addition leads to decrease of spherulite

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size.[15,16] In this work polypropylene hollow fiber membranes were fabricated via combination of TIPS and stretching process. Effects of NA on the crystallization kinetics and membrane structure were investigated in terms of phase separation mechanism and stretching.

Experimental

Materials. Isotactic polypropylene (iPP) (Daehan Yuhwa Co, 5012) with melt flow index of 2.0 g/10 min was used in this work for the hollow fiber membrane formation. Soybean oil from Cheil-Jedang Co. was selected as a diluent for iPP. Freon141B from Dong-Yeon Co. was used to extract diluent from hollow fiber membrane and Tween-80(Aldrich Co.) was used to hydrophilize the surface and inner pore of the membrane. NA's used in this work are adipic acid (AA, Aldrich Co.), benzoic acid (BA Aldrich Co.), and dibenzylidenesorbitol. (Ciba Geigi Co.) All the chemicals in this work were used as received with no further purification.

Preparation of Polypropylene Hollow Fiber Membrane and Module. Polypropylene hollow fiber membranes were prepared by using the same apparatus as reported in previous work.[4] Melt spinning was conducted at a constant feed rate of 2.17 mL/min to spinneret with outside diameter of 5 mm and inside diameter of 2 mm. Melt spun hollow fiber was solidified in the air without coagulation bath and stretched between the rollers at different speeds before it was wound on a bobbin. Air gap, defined as the distance between spinneret and the first roller, was set as 117 cm and draw ratio, defined as the ratio of linear velocity at winder to that at spinneret, was optimized as 528. Spinning temperature was 158 °C. Hollow fiber membranes were potted with epoxy resin in polymethylmethacrylate (PMMA) tube to make a test module. Hydrophobic poly-propylene hollow fiber membrane was hydrophilized with 20 vol% Tween-80 aqueous solution for 30 minutes and was rinsed with pure water for 15 minutes prior to test.

Membrane Characterization. Differential scanning calorimeter (DSC, Perkin-Elmer, DSC-7) used to characterize the crystallization kinetics for iPP-soybean oil system. Samples were prepared by melt blending iPP, diluent and NA at a specified composion in a flask with a mechanical stirrer under nitrogen atmosphere at 210 °C for 4 hrs. The melt-blended sample was quenched into ice water to retain the uniform composition without segregation by slow cooling. Measured amount of sample was loaded in DSC and kept at 210 °C for 10 minutes in order to remove the previous thermal history of the sample. For non-isothermal crystallization it was cooled at 10 °C/min scanning rate and exotherm peak for crystallization was obtained, and further calculations were performed for the characterization of crystallization kinetics. For isothermal crystallization the sample was quenched to a specified crystallization temperature as the instrument permitted, 200 °C/min. Thus gained isothermal
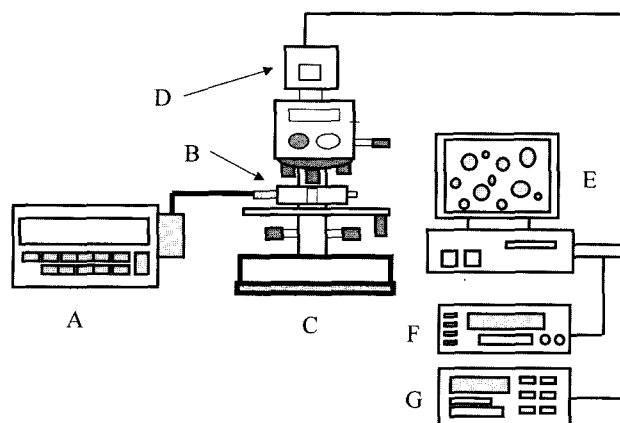

Figure 1. Thermo-optical microscope system (A: Central Processor, B: Hot stage, C: Optical microscope, D: CCD camera, E: Image analyzer, F: VCR recorder, G: Color video printer).

crystallization curves were analyzed to determine the completion time and peak time of isothermal crystallization.

Thermo-optical microscope system was composed of optical microscope (Zeiss, Jenaval), central processor (Mettler, FP-90), and hot stage (Mettler, FP-82) as shown in Figure 1. Image was captured by CCD camera and was analyzed by an image analyzer system (IP win). Thin slice of solid sample was placed between the cover silps sealed with Teflon tape and grease. The sample was mounted on a hot stage at 210 °C and kept for 10 minutes in order to remove the thermal history. Then it was switched to another stage at 115 °C in order to obtain the phase separation and crystallization images. Continuous images were captured and recorded, and spherulite growth was characterized. Surface and cross sectional images of hollow fiber membranes were examined by a scanning electron microscope (SEM: Leica, Stereoscan 440).

Water flux and bubble point pressure measurements were performed by the conventional methods.[4] Tensile strength was measure with universal testing machine (Toyo Bald Win) at a crosshead speed of 1 cm/min.

Results and Discussions

Effect of Kinds of Nucleating Agent. Each NA was characterized by nonisothermal and isothermal crystallization tests by DSC. 1 wt % of each NA was added to iPP/soybean oil system (40/60), and it was scanned at a cooling rate of 10 °C/min for nonisothermal crystallization and it was quenched to 115 °C for isothermal crystallization. As shown in Table I crystallization temperature for non-isothermal crystallization was elevated by the addition of each NA when compared with that of non-nucleated sample. Peak time and completion time for isothermal crystallization was much reduced by the addition of NA, which means the acceleration of crystallization by NA. It was confirmed that each NA

Table I. Crystallization Characteristics of Each Nucleating Agent in iPP/soybean Oil System

Nucleating Agents	No NA	Benzoic acid (BA)	Adipic acid (AA)	Dibenzylidene sorbitol (DBS)
Crystallization Temperature at 10 °C/min Cooling	105.34 °C	118.33 °C	116.33 °C	107.99 °C
Peak Time during Isothermal Crystallization at 115 °C	3.16 min	0.06 min	0.06 min	1.01 min
Completion Time during Isothermal Crystallization at 115 °C	6.54 min	0.26 min	0.27 min	3.01 min

Composition of NA = 1.0 wt%.

used in this work has nucleation effect by the results shown in Table I. Each NA has its own nucleating power, and BA is the most effective while DVB was not as effective as the others

Spherulite growth was examined for each nucleated sample during the isothermal crystallization at 115 °C by using thermo-optical microscope. Crystallization temperature was selected based on the experimental time scale and the image visualization, though it is not same as that of thermal analysis. As shown in Figure 2, spherulites of non-nucleated sample and DBS added sample kept growing during the time span shown in Figure 2. They kept growing for more than an hour to reach the final size of 306 μm (1 hr 10 min) for DBS added sample and 318 μm (1 hr 30 min) for non-nucleated sample. However, spherulites for BA and AA added samples reached a limiting size (17 μm for BA and 28 μm for AA) and no more growth was detected. Nucleated samples with BA and AA had greater number of nuclei and spheru-
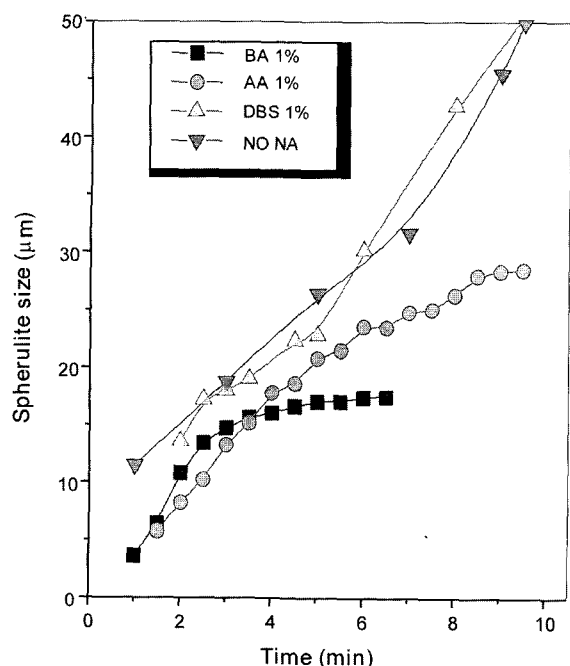
lites than non-nucleated and DBS nucleated samples, and increase of number of spherulite caused the early spherulite impingement on each other, which limited the growth.

Polypropylene hollow fiber membranes were prepared by the melt spinning and cold stretching process with the same composition as those for DSC and thermo-optical microscope tests. It is nearly impossible to trace the temperature of hollow fiber after spinning, and we could not apply the same cooling condition to thermal and optical analyses as that of real fiber spinning. However, trends obtained from thermal and optical analyses could be applied to real fiber spinning. Figure 3 showed the outer surface image of hollow fiber membranes prepared with different NA's. BA and AA added samples showed more porous structures than non-nucleated and DBS added samples. Microfibrils were much developed in the nucleated samples, which were caused by stretching process. Since BA and AA added sample had higher crystallization temperatures and began to crystallize or solidify much earlier than non-nucleated and DBS added samples, the formers had more chance to be stretched during the spinning. Size difference in spherulites also made the contributions in increase of number of site for stretching, that is, amorphous region between the spherulites. It was confirmed that formation of homogeneous microporous structure with microfibrils were enhanced by the addition of BA and AA. DBS had no significant effect on stretching, because it had the least nucleating effect. It showed somewhat more dense structure than non-nucleated one. Cross sectional image of each membrane is shown in Figure 4, and BA and AA added samples have more porous structures than the others as is the trend of outer surface structure.

BA and AA added sample showed greater flux than non-nucleated and DBS added ones as shown in Figure 5, which is in agreement with the structures shown in Figures 3 and 4. Maximum pore size of each membrane was determined by bubble point pressure measurement as described in previous work,[4] and it is in exactly the same trend as those of structure and pure water flux as shown in Figure 6. More nucleated sample has greater pore size as well as greater porosity. Increase of number of spherulites by NA addition secured the more site for the stretching to make micropores. Tensile strength of each fiber was tested (Figure 7), and BA and AA added samples were weaker than non-nucleated one, which
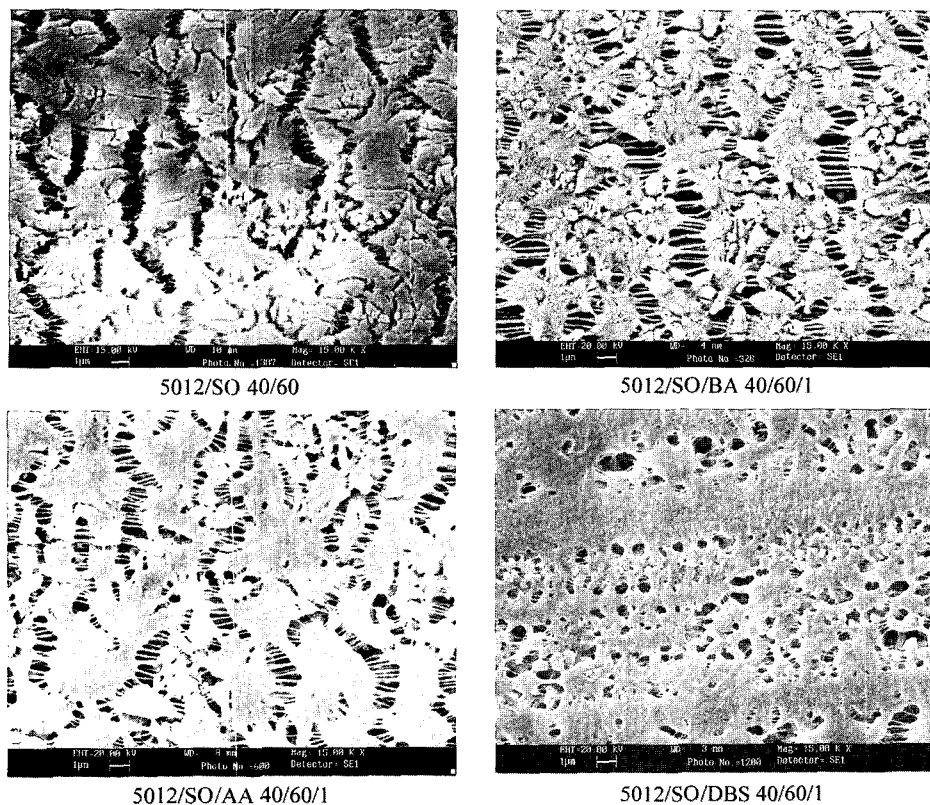

Figure 2. Characteristics for spherulite growth with different nucleating agent at 130 °C (5012/SO/NA = 40/60/1).

5012/SO 40/60

5012/SO/BA 40/60/1

5012/SO/AA 40/60/1

5012/SO/DBS 40/60/1

Figure 3. Outer surface images of iPP hollow fiber membranes with different nucleating agents.

5012/SO 40/60

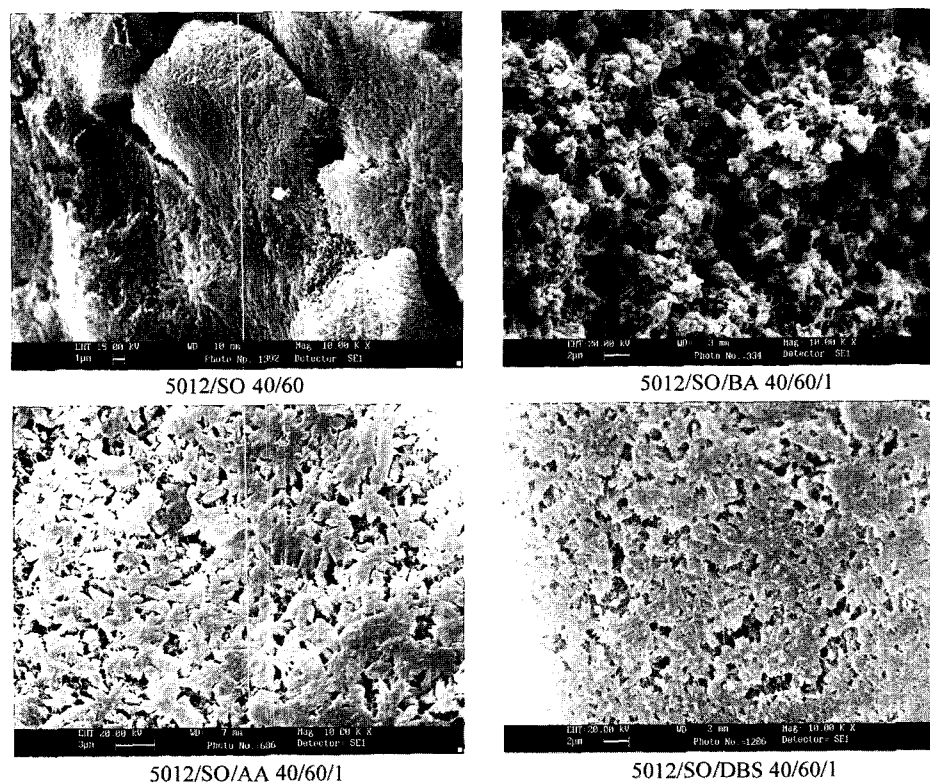5012/SO/BA 40/60/1

5012/SO/AA 40/60/1

5012/SO/DBS 40/60/1

Figure 4. Cross sectional images of iPP hollow fiber membranes with different nucleating agents.

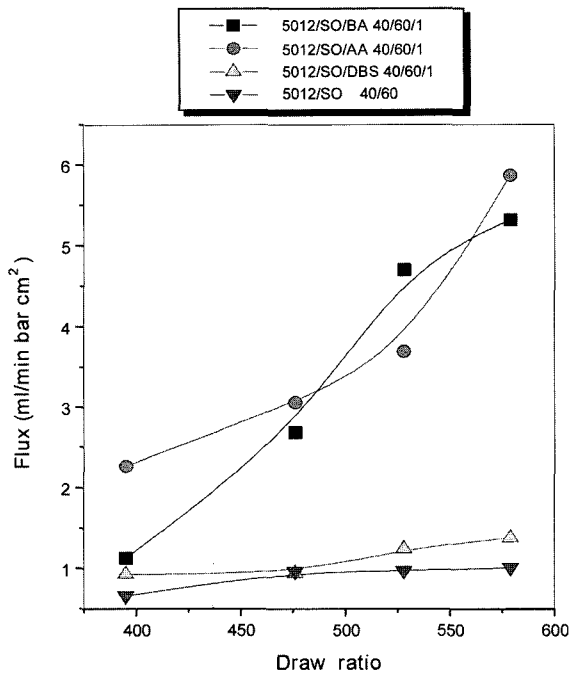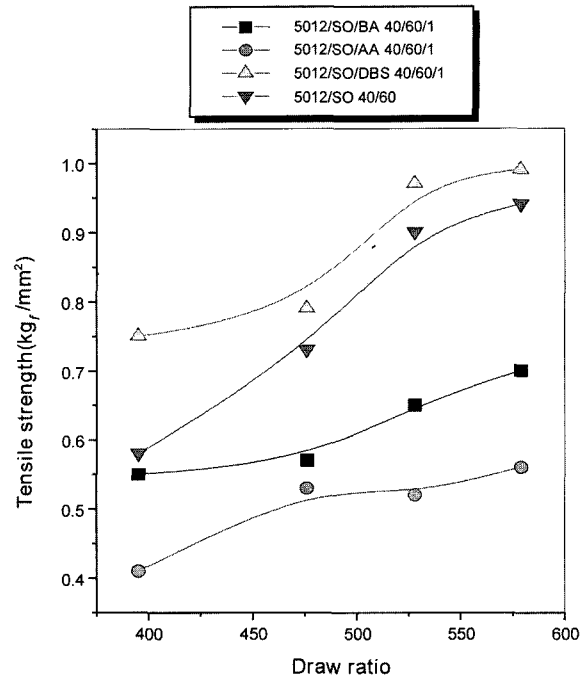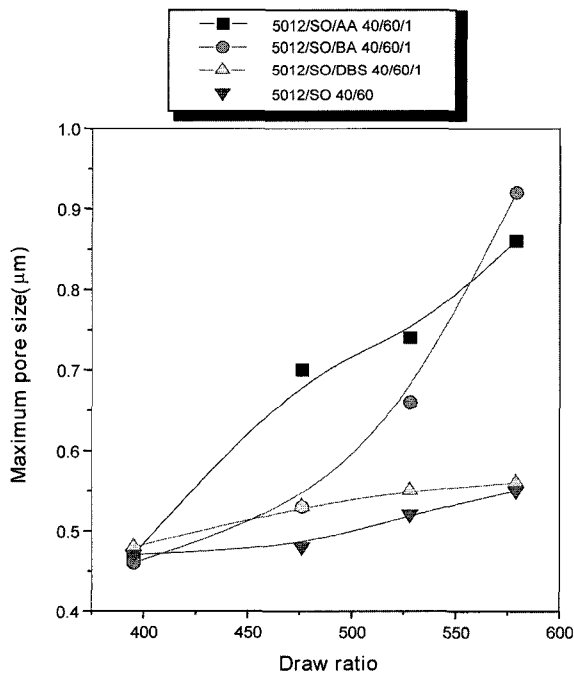**Figure 5.** Water flux of iPP hollow fiber membranes with different nucleating agents.

Figure 6. Maximum pore size of iPP hollow fiber membranes with different nucleating agents.

Figure 7. Tensile strength of iPP hollow fiber membranes with different nucleating agents.

Figure 8. Effect of benzoic acid composition on crystallization temperature at 10 °C/min cooling rate.

was expected from the high porosity. DBS added sample showed the greatest tensile strength among all the samples tested. As shown in Figure 3, DBS added sample has dense surface structure, which contributed the increase of tensile

strength of the sample. Though DBS was not an effective NA when compared with BA and AA, it helped the membrane be more dense and stretchable. DBS added fiber has greater degree of stretching than even the nonnucleated one.

Effect of Composition of Nucleating Agent. BA was proved to be the most effective NA among the NA's tested in this work and it was selected for the further works. Effect of
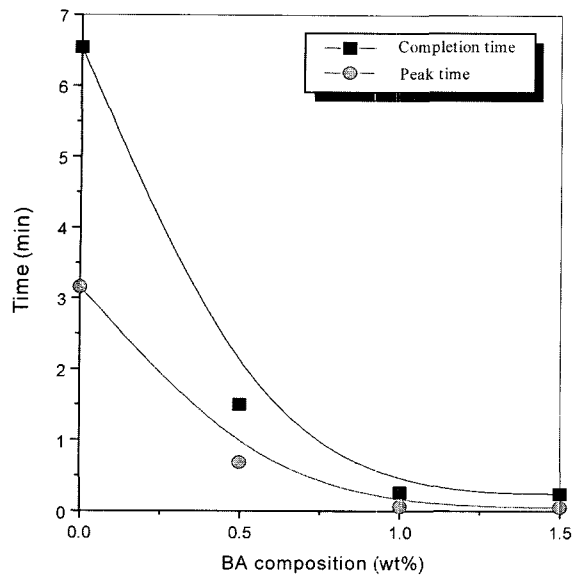
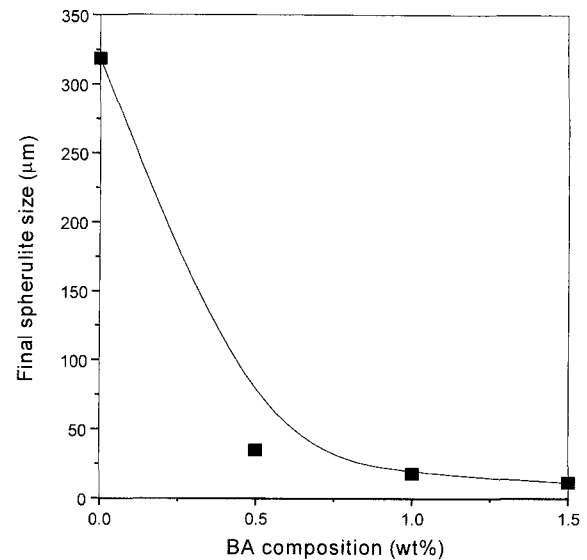Figure 9. Effect of benzoic acid composition on isothermal crystallization at 115°C.

Figure 11. Effect of benzoic acid composition on the final spherulite size for isothermal crystallization at 130°C.
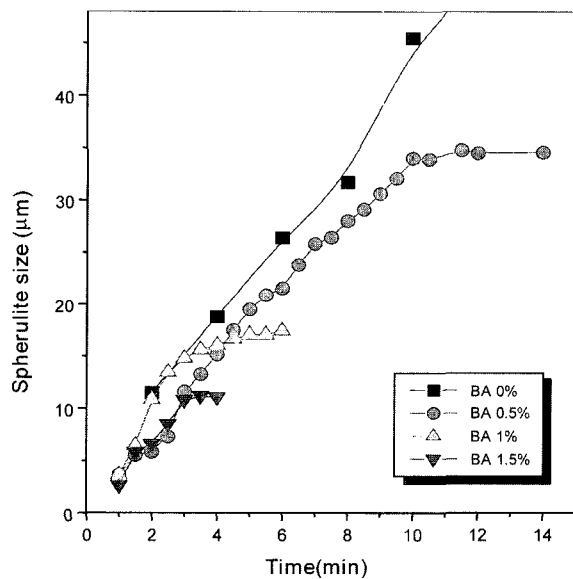

Figure 10. Effect of benzoic acid composition on isothermal spherulite growth at 130°C.

BA composition was examined by changing the composition from 0 to 1.5 wt%. As shown in Figure 8, non-isothermal crystallization temperature at 10°C/min cooling rate increased with the amount of BA added, though the increasing rate decreased at higher BA composition. Peak time and completion time for crystallization decreased with BA composition increase as shown in Figure 9. Increase of BA composition resulted in the higher nucleation density, and reduced the chain fold energy to accelerate the crystallization. Spherulite growth was much affected by the amount of

BA added as shown in Figure 10. Increase of BA caused high population of nuclei and induced the early spherulite impingement to cease the growth. Spherulite size of BA added sample was much reduced when compared with that of nonnucleated one. Initial 0.5 wt% of BA much reduced the spherulite size to 1/8 of that of nonnucleated one as shown in Figure 11. Additional amount of BA had much less nucleation effect than the initial 0.5 wt% dose.

Figure 12 showed the outer surface image change with the increase of BA composition. Increase of BA amount resulted in highly microporous structure formed by offering the increase of number of amorphous site for stretching. Increase of porosity by the addition of BA enhanced the water flux of the membrane as shown in Figure 13. Maximum pore size was also affected by BA composition as shown in Figure 14, which was in good agreement with the surface structure examination by SEM as shown in Figure 12.

Conclusions

NA accelerated the crystallization by increasing the nucleation density and reducing the chain fold energy. DSC works proved that NA played a role in elevating the crystallization temperature and increasing the crystallization rate. Thermo-optical microscope works revealed that number of spherulites was increased to result in the early impingement by the addition of NA, which ceased the spherulite growth. Increase of number of spherulite offered more inter-spherulitic amorphous sites for stretching to result in higher porosity as well as greater pore size. Therefore, addition of NA to polymer/diluent system for hollow fiber spinning enhanced the flux and maximum pore size. NA also helped the sample
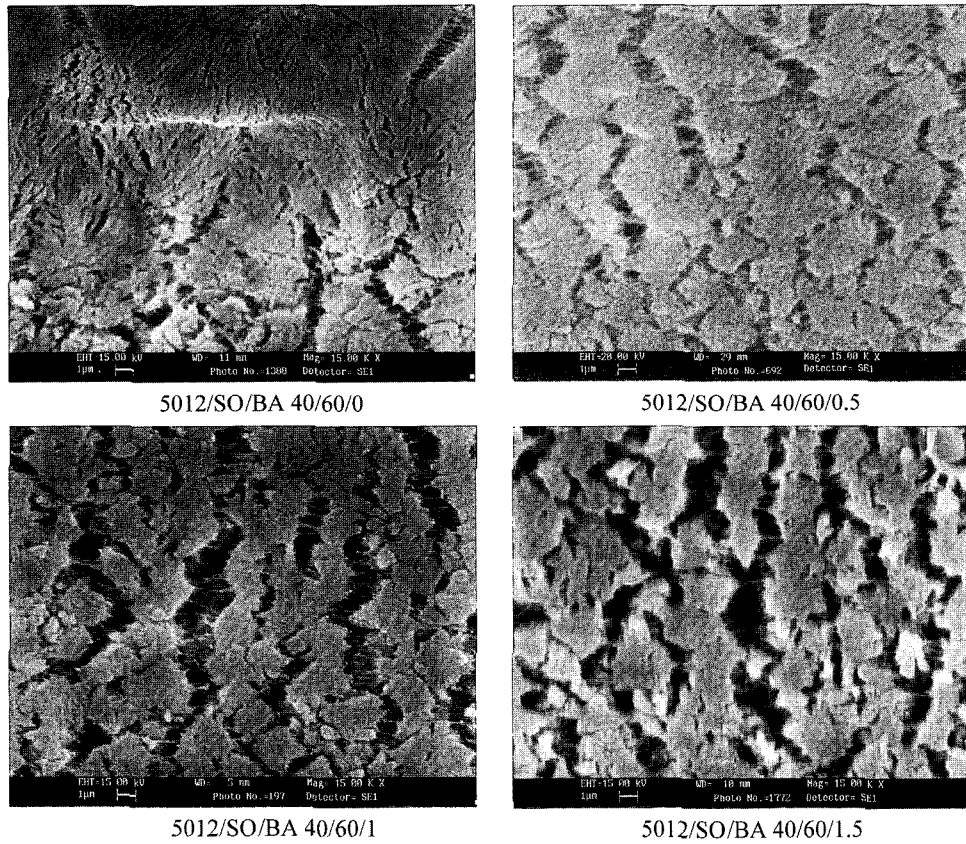
5012/SO/BA 40/60/0

5012/SO/BA 40/60/0.5

5012/SO/BA 40/60/1

5012/SO/BA 40/60/1.5

Figure 12. Inner surface images of iPP hollow fiber membrane with different benzoic acid composition.
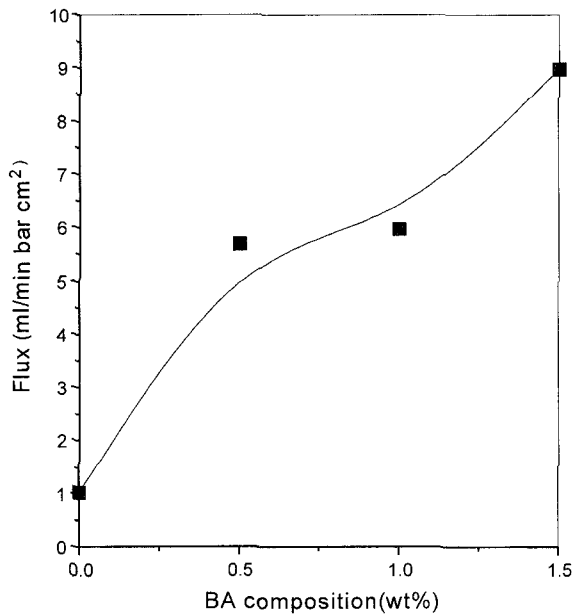

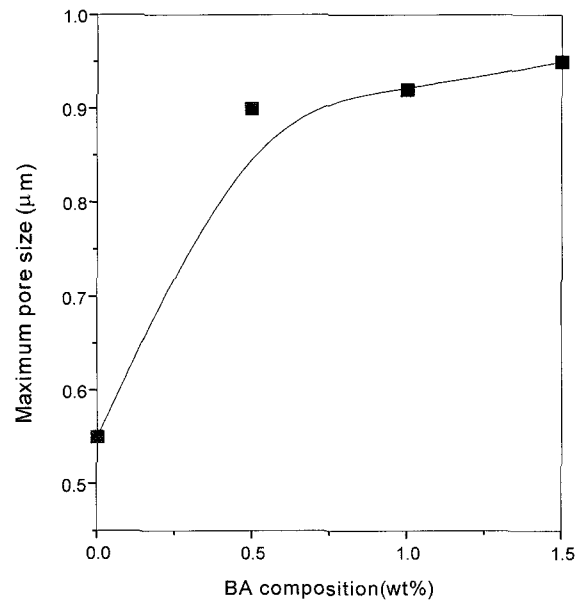**Figure 13.** Flux of iPP hollow fiber membranes with different benzoic acid composition.

Figure 14. Maximum pore size of iPP hollow fiber membranes with different benzoic acid composition.

have uniform microporous structure. BA and AA showed the appreciable nucleating effect, while DBS was less effective

than those. Mechanical strength of hollow fiber membrane was reduced by the addition of BA and AA due to the

increase of porosity. DBS added sample showed the greater tensile strength than even the non-nucleated one, though it was not an effective NA. Increase of BA composition caused high population of nuclei and spherulites, and it helped increase the porosity and flux of the membrane. Increase of nucleation effect at high composition of BA was not as great as that at low composition, and there may be a saturation point for BA addition. Addition of NA in the melt spinning of iPP hollow fiber membrane affected the crystallization kinetics and stretching to attain the better performance of the membrane.

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